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THERMAL BEHAVIOR OF SOME LONG-CHAIN QUATERNARY AMMONIUM SALTS

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ABSTRACT

In the present work the synthesis and thermal behavior of some long - chain quaternary ammonium salts functionalized in the polar head, of the formula $C_{12}H_{25}\overset{+}{N}(CH_3)_2RBr^-$, are reported. It has been found that these salts form, through a solid-solid transition, a peculiar solid phase of liquid-like character and they also exhibit improved thermal stability compared to non-functionalized n-alkyltrimethylammonium bromides. Furthermore the thermodynamic parameters of these compounds are dependent in a complicated way on the nature of the functional group.

INTRODUCTION

According to some recent reports[1-8] certain amphiphilic compounds form layered structures in the solid phase. On heating, these compounds show a multiple-step melting behavior with their layered structures more or less preserved. This leads to the formation of some peculiar solid polymorphs - with analogies to smectic mesophases - and smectic phases which at the clearing point are transformed to isotropic melts.

Long-chain quaternary ammonium salts, dealt in this study, which exhibit such behavior[3,4], form layered crystalline structures[3] through the electrostatic interaction of quaternary centers with halide anions. This interaction leads to the creation of bidimensional polar layers sandwiched between the long alkyl chain layers. Upon heating these quaternaries are transformed, through a solid-solid phase transition, to another layered structure, viewed as a mesophase[3] in which although the hydrocarbon chains are "melted"(conformational melting) the ionic bonding inside the polar layers remains practically intact. Thus free molecular motion of the amphiphiles is prevented by the rigidity of the ionic layers. It has also been found that n-alkyltrimethylammonium halides decompose after the clearing point in the presence of nitrogen[3] or even before the clearing point in atmospheric oxygen. In the course of the synthesis of functionalized quaternary ammonium salts of the formula:

$CH_3(CH_2)_{11}\overset{+}{N}(CH_3)_2R\,Br^-$ ($R=CH_2CH_3$, $CH_2CH_2CH_3$, CH_2CH_2OH, $CH_2CH_2CH_2OH$, CH_2COOH, CH_2CH_2COOH, $CH_2CH_2CH_2CN$, CH_2COOCH_3, $CH_2COOCH_2CH_2OH$) we have found that certain of these quaternaries exhibit good thermal stability even when heated in the

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presence of atmospheric oxygen[4]. They also modify the micellar properties[9] of non-functionalized micelles.

In this communication we limit our investigation on the thermal behavior of the members with R=CH_2CH_3(I), $CH_2CH_2CH_2OH$(II), $CH_2CH_2CH_2CN$(III), CH_2COOH(IV), CH_2CH_2COOH(V), which show satisfactory thermal stability and well-resolved transitions.

METHODS

The quaternary ammonium salts were prepared by the interaction of dimethyldodecylamine with the appropriate bromide in ethyl acetate, a medium in which the reaction proceeds relatively fast and crystalline material is obtained[10]. The resulting salts were recrystallized twice from ethyl acetate, dried in vacuum over phosphorous pentoxide, and their purity was confirmed by C, H and N elemental analysis. All"solid mesophases" reported here were observed by optical microscopy on a Reichert Thermopan polarizing microscope equipped with a camera.

Differential scanning calorimetric curves (Fig.), at 10°C/min, were recorded with a Du Pont 910 DSC equipped with a R90 Temperature Programmer. The transition enthalpies were obtained by using as the reference standard a sample of indium. Under the experimental conditions the precision of the reported parameters was of the order of 2%.

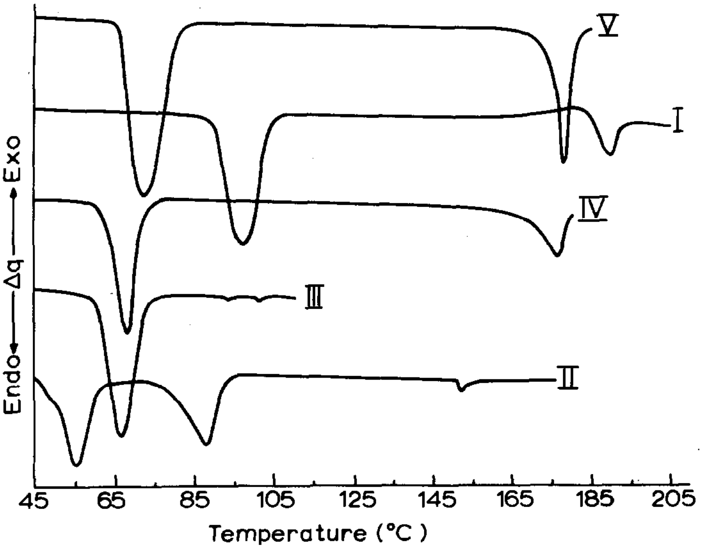

Fig. DSC traces of compounds I to V

RESULTS AND DISCUSSION

The introduction of functional groups through quaternization of single-chain tertiary amines is a facile process and functionalization is determined by the availability of the corresponding halides. The functionalized quaternary ammonium salts investigated in this study are listed in Table 1 along with their thermodynamic parameters.

According to the previously discussed layered structure of these compounds the low temperature phase transition is attributed to the conformational melting of the long aliphatic chains, leading to a disordered layered solid state. This peculiar solid structure and the fact that the melted aliphatic chains occupy considerably larger molar volume than the rigid polar layers accounts for the liquid-like appearance of these salts above the first transition temperature, as observed by optical microscopy.

Table 1. Transition Temperatures, Enthalpies and Entropies obtained by DSC for the functionalized quaternary ammonium salts.

	First heating run			Second heating run			Third heating run		
R	T_{tr} K	ΔH kJ/mol	ΔS J/Kmol	T_{tr} K	ΔH kJ/mol	ΔS J/Kmol	T_{tr} K	ΔH kJ/mol	ΔS J/Kmol
I	362	38.9	107.4	345	30.9	89.6	336	24.9	74.1
	455	6.5	14.2	439	4.5	10.2	434	3.7	8.5
II	322	14.9	46.3	321	14.9	46.4	321	14.9	46.5
	349	14.5	41.4	345	13.3	38.6	344	12.7	36.9
	424	0.83	1.95	423	0.67	1.58	423	0.63	1.5
III	332	40.1	120.8	332	39.5	118.9	332	39.7	119.5
	365 373	0.73	1.96	365 373	0.66	1.8	366 372	0.65	1.77
IV	334.5	30.2	90.2	334	28.3	84.7	334	28.2	84.6
	441	16.7	37.9	438	14.1	32.2	437	13.1	30.0
V	338.5	46.6	137.8	337	43.6	129.3	337.	43.1	127.8
	447	18.9	42.2	445	17.9	40.2	445	17.2	38.7

The data of Table 1 indicate that although all quaternaries contain a twelve carbon aliphatic chain they demonstrate significant differences even in the thermodynamic parameters of their first transition corresponding to the conformational melting of the long chains. This is evidence that the introduction of the functional group on the polar head of the molecule modifies the crystal structure and through that the van der Waals and ionic forces in the lattice. Although the obvious trend in the thermal behavior among the derivatives of Table 1 does not seem to exist, it is nevertheless obvious that the introduction of the functional group weakens the lattice interactions so that the observed phase transitions require less energy than the corresponding transitions in the non-functionalized derivative. This is in accordance with the observation that the functionalized salts do not decompose. With the exception of the ethyl derivative which undergoes only slight decomposition in the presence of atmospheric oxygen, all the other derivatives of Table 1 are remarkably stable through several heating-cooling runs.

Another conclusion deduced from the thermodynamic data of Table 1 is that a significant degree of the organization in the lattice is lost during the conformational melting of the aliphatic chains, although the carboxylic derivatives appear to retain a higher degree of order above the first transition than the other derivatives.

The hydroxy derivative exhibits instead of one two phase transitions below its clearing temperature. We have ascribed the first change to a crystallographic phase transition because it does not appear in a second heating run unless it takes place at least 40 hours after the original heating run. This means that at the first transition ($322^{0}K$) the hydroxy derivative undergoes a crystallographic change while the reestablishment of the original crystal structure upon cooling is a slow process. Similar behavior has been reported in the literature for this type of salts[3].

In conclusion, the introduction of functional groups on the polar head of the quaternaries affect in a complicated way the thermodynamic parameters and in many cases they enhance their thermal stability.

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